BOOK OF PROCEEDINGS

WASTES

solutions treatments opportunities

2013 2nd braga 11 > 13 september

International Conference

Book of proceedings

2nd International Conference: WASTES:Solutions, Treatments and Opportunities

EDITION
CVR - Centro para a Valorização de
Resíduos

EDITORS
Fernando Castro, Cândida Vilarinho, Joana Carvalho,
Alexandra Castro, Jorge Araújo, Alexandra Pedro.

COVER DESIGN
Rui Ferreira

ISSN
2183-0568

250 Copies
september 2013

CVR - Centro para a Valorização de Residuos
Campus de Azurém da Universidade do Minho
4800-058 Guimarães
PORTUGAL

Telef.: +351 253 510 020
Fax: +351 253 510 029
http://www.cvresiduos.pt
e-mail: geral@cvresiduos.pt

REMEDIATION OF CRUDE OIL CONTAMINATED SOILS BY MEANS OF BITUMEN EMULSIONS.

M.T. Viñas[1] and A. Páez[2]
1 Universidad Politécnica de Madrid. Cardenal Cisneros 3. 28040 Madrid. mteresa.vinas@upm.es
2 Repsol (CTR) Ctra. Extremadura km 18.28935 Madrid. apáezd@gmail.com

ABSTRACT

Effective remediation of contaminated sites with oils, heavy metals and other chemical agents is one of the most important environmental problems all over the world. Contaminated soils by petroleum from different sites and origins, might contaminate groundwater aquifers and then be spread by rain. Many years and the requirement of remedial techniques may be needed to remediate them. However, previous experiences show the uselessness of these methods for the solution of all problems. As any case of soil contamination is different, specific studies with relevant factors at financial aspects, legal limits and waste and soil characteristics are needed. In this work, a study of the use of bitumen asphalt emulsion to remediate contaminated soils by crude oils is exposed. By means of the soil stabilization technology, using the contaminated soils as aggregates and the tailor made emulsion as binder, the feasibility of the mix application to produce stable and resistant pavements is demonstrated

Keywords: Contaminated soil; Bitumen emulsion; Remediation

INTRODUCTION

Effective remediation of contaminated sites with oils, weight metals, etc., is one of the most important ecological problems all over the world. The contaminant substance, from industrial or human activity, could contaminated groundwater aquifers and then be extended by rain. It may take years of efforts to remediate them. To avoid this problem, the application of remediation techniques has been essayed. However the experience gained with these techniques has proved their limitations and has showed that they are not capable of solving some problems like time necessary for remediation, limit efficacy of treatment, high cost of remediation and no-incentives to restoring contaminated soils. The conclusions is that each case of soil pollution is different and the way of manage it requires study relevant factors like waste and soil characteristics, financial aspects and legal limits admitted in each area.

Hydrocarbon-contaminated soils (HCS) can be found in places where petroleum is managed: storage areas (crude oil or derivate products), refineries or oil wells, transport systems (oil pipeline, charge y discharge plants,) and distribution places such as gas stations or airports. Remediation techniques usually applied to HCS includes monitored natural attenuation, in situ soil vapour extraction, in situ steam injection vapour extraction, air sparging, pump and treat, in situ bioremediation, vacuum-enhanced pump and treat [1]. Current site remediation techniques have many limitations associated with them and site contaminated with organic pollutants may never be restored to its conditions prior to pollution.

In USA and many other countries with such increase of HCS, Environmental Protection Agency (EPA) has promoted using of alternative technologies (ATE) to remediate HCS, mainly in leaking and spilling underground storage tanks. One of this ATE's is the application of a well-known technique, soils stabilization (SST), to soils remediation.

Soils Stabilization

In last years , several studies present the soil stabilization using HCS as remediation technology [2, 3, 4, 5, 6, 7] This ATE is used to recycling petroleum contaminated soils that could be used like aggregate in light traffic road construction. The objectives of this technology are being able to:

- produce impermeable pavements and avoid contaminant leaching and dispersion by rain (soil remediation).
- produce pavements with high strength to traffic and deformation.

Soils stabilization techniques used actually to get these objectives includes:

- *Granulometric stabilization*.- Consist in mix granulated materials (including contaminated soil and natural soil) that provided cohesion and clayed silt material like waterproof binder. This new soil is extended and compacted with watering. This SST does not avoid the mobility of the organic contaminants by rain.
- *Stabilization with Portland cement*.- Contaminated and no-contaminated soil is mixed in-situ with cement, extended and compacted with water in the closely-controlled proportions. It's largely used SST *but more expensive that the first one.*
- *Stabilization with lime*.- Homogeneous and compacted mixture of loamy soil, lime and water can be used in stabilized soil in rural roads.
- *Stabilization with bitumen*.- Hot mix asphalt mixtures have been used to get stabilized soils using contaminated soils like aggregate. Bitumen is known to be a durable, flexible, adhesive, inert binder with good water resistance and capsulation properties that could avoid the contaminant transport and supply a durable and creep resistant light traffic surface by stabilization. Hot mix asphalt mixtures have been used in soils stabilization like an ATE to remediate HCS with good results in durability, strength and permeability [8]. This technology is cheaper than others like incineration and quicker than, for example, bioremediation. But it needs a very specific equipments and plants and requires the transport of soils to the plant.

One of the limitations of the stabilization of contaminated soils with hot bitumen is that it needs an expensive plant to manufacture the hot and very complicated equipment to landing it. In addition these plants are frequently implanted far away from the places where the contaminated soils are located. This fact signifies an additional expense to the treatment.

There is feasible bitumen based alternative to the stabilization of soils with hot bitumen that is the use of bitumen emulsions. This is named the *cold technology*. To use this technology only is needed a very simple and inexpensive equipment. In addition the plants can be built near the contaminated soils places.

In this work an evaluation of the *cold technology* is done. The soils were obtained from the south of Argentina and were contaminated by the crude oil produced in that zone.

OBJECTIVE

The main objective of this paper is to study the feasibility of using cold asphalt technology like SST to built light traffic roads using HCS like aggregate.

In emulsion technology, contaminated soil is mixed with bitumen emulsion. The bitumen emulsion is tailored specifically to the material in question. Prior to placement, the product is cured by allowing water to evaporate after the breaking of emulsion when mixed with aggregate.

This process is used on site at an ambient temperature with cold stone material. The cold process ensures that the emission of volatile hydrocarbons is minimised and includes two possible processes:

-Mixing with a rather simple plant, very easy to transport, with a feeder and a mixer.

-Mixing in situ with the adequate machinery.

Bitumen emulsion (also lime and cement) can be used as binder. The mix can be stored in a silo before lying. These mixtures, extended and compacted, supply an excellent base layer in light traffic roads construction or no-dust or impermeable layer in rural roads. The bitumen after the breaking of emulsion plays the role of an encapsulating agent for the hydrocarbons that contaminate the soil.

METHODS

The experimental process tries to decide if the use of HCS like aggregate in rural or light traffic road construction in a stabilization process with bitumen emulsion (cold technology) is an effective remedial technique and produces stable and resistant pavements. In order to clarify these aspects, research is designed in three steps:

- Quantifying the soil pollution problem.
- Verifying that this technology is able to encapsulate the hydrocarbon contaminant product and avoid its transport.
- Measuring properties of the pavements.

HCS characterization.

Test was conducted in accordance with NLT tests (Spanish Road Studies Centre) with correspondence at ASTM tests. *In the first step* contaminant is separated from soil with solvent and then quantified (without volatile hydrocarbons). Hydrocarbons obtained are distilled and then characterized measuring density or another technical property. Separated soil is tested for grain size distribution. Test methods are shown in table 1.

Measure contaminant capability of the HCS and the HCS stabilized.

In order to investigate contaminant capability of the HCS and the HCS like aggregate mixed with bitumen, by natural leaching and dispersion with rain water, a leaching non normalized method was used. This method is usually found in asphalt laboratories for intensive lixiviation of asphalt mixes. The extraction on both HCS and HCS mixed with asphalt emulsion, performed by distilled water acidulated with acetic acid (pH = 5), refluxing for 24 hours, makes possible detect contaminant agents (metals, total organic compounds and hydrocarbons) on the extract. This extract was analysed using the following methods: metals with atomic absorption spectrophotometer and total organic compounds and hydrocarbons with infrared spectroscopy (EPA 0418.1)

Measure properties of the pavements.

Different mix designs are prepared to obtain valid data from the experimental test. First of all, cement is used as a stabilizer in order to compare results because it is mainly used at this moment.

Then bitumen emulsion is employed as alternative binder to cement. Cement provides stability and strength to the mix and bitumen emulsion encapsulates contaminants and also provides flexibility to the pavement. Both stabilizers are used mixed or separately and the mix must be tailored specifically to the material to be stabilized.

A test is selected to investigate the improvement of mechanical properties of pavement stabilized with bitumen emulsion in specimens just prepared and exposed to water effect. This test is the immersion-axial compression test [9,10]

This standard test method determines loss of strength because of loss of cohesion by water immersion in compacted bituminous mixes. Two sets of specimens are prepared and compacted (NLT161, ASTM D 1074-02): the first one is submerged in a water tank for 4 days at 49ºC (NLT162, ASTM D 1075-96) and the second one is exposed to air at the same time (NLT161, ASTM D 1074-02). Specimens are then tested for compressive strength and density (NLT-168, ASTM D 1188, 2726, 3203-96). The effects of water in loss of strength are obtained by comparing the resistances (R) before and after immersion in water by means of expression:

$$\text{Conserved strength (\%)} = \frac{R_{\text{after immersion}}}{R_{\text{before immersion}}} \times 100$$

There is no specification for the minimum resistance required in the results of this test. However the experience shows that a minimum value of compressive strength before immersion should be 4.32 Kg/cm^2 and the compressive strength has to be at least 50%.

EXPERIMENTAL RESULTS

Hydrocarbon-contaminated soils (HCS) can be obtained from different places where petroleum is managed and then they have different contaminant composition to determine. In this paper has been studied two HCS, obtained from places where the crude oil is produced in the South of Argentina:

Sample 1.- soils with clean-up of petroleum tanks

Sample 2.- soil with petroleum spills

both of them from atmospheric storage tank (disposal sites).This HCS to remediate are used as aggregate in cement concrete in rural roads with next problems: contamination of groundwater aquifers by lixiviation or leaching (hydrocarbons are extended by rain) and short durability of cement pavement.

Table 1.- Hydrocarbons content and density

	Sample 1	*Sample 2*
Hydrocarbon content based on sample. [%] (NLT – 164).	2.36	10.64
Hydrocarbon content based on aggregate. [%] (NLT – 164).	2.41	11.90
Relative density [25ºC] (NLT – 122).	1.016	1.008

These samples were extracted to study the hydrocarbons content and their consistence. Table 1 present the data obtained in the extraction of the contaminated soils.

Extracted Hydrocarbons are a black liquid (petroleum probably) too much flowing at room temperature to determine consistence by penetration test. Different relative density is a consequence of different disposal sites and composition. *Sample 2* (spills) have more hydrocarbons content.

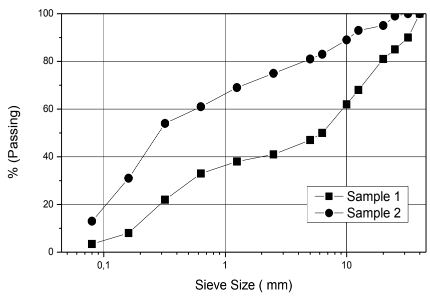

Figure 1.- Grain size distribution for the PCS. (NLT – 165).

Grain size distribution after extraction presented in fig. 1 show that *sample 2* (spills) have high content on fines than *sample 1* but, even though two samples had a very wide grain size distribution, both falls into the range of allowable specifications.

After been characterizes, samples were mixed with selected binder to study pavement strength. Selected binder is a bitumen slow setting emulsion with next formulation: Bitumen 80/100 (61%wt), Tallow Polyamide (0,50 %wt), Tallow Imidozoline (0,10 %wt), HCl (0,75 %wt),Water (up to 37,65%wt)

Some specimens for immersion-compression test have been prepared only with bitumen emulsion but resulting cohesion was very poor. This phenomenon is probably due that natural filler from the sands do not produce adequate mastic with the bitumen of the emulsion. To increase the strength the addition of cement or hydraulic lime prior the mix with bitumen emulsion was evaluated.

Table 2 **-** Results of immersion-axial compression test with Sample1 (soils with clean-up of petroleum tanks) (NLT – 162 y 161).

Curing 24 h at room temperature and 4 days at 60ºC. Immersion procedure nº 1, 4 days at 49ºC									
Identification	1	2	3	4	5	6	7	8	9
PROPORTIONS									
i. Sample 1	100	100	100	100	100	100	100	100	100*
Emulsion	3	4	5	5	3	4	5		
Lime	1.5	1.5	1.5						
Cement					2	2	2	2	2*
Water	2.0	1.6	1.2	1.2	2.0	1.6	1.2	3.0	3.0*
Dry strength, [kg/cm^2]	19.56	11.65	13.34	4.8	21.39	18.97	15.06	7.14	7.74
After immersion strength, [kg/cm^2]	6.16	3.72	3.98	0.5	14.53	11.97	8.59	8.2	
Conserved strength, [%]	31	32	30	10	68	63	57	115	
Relative Density [s.s.s.]	2.205	2.164	2.171	2.080	2.193	2.175	2.162	2.215	2.210

* These specimens were cured in wet chamber at 25ºC, 95% relative humidity for 7 days.

Table 2 and 3 show the results obtained from the immersion-compression tests; less difference of strength after and before immersion indicates better adhesively bitumen – aggregate. This test also determine minimum emulsion amount to get optimal mechanical strength of dense cold mixes.

Data presented in table 2 (soils with clean-up of petroleum tanks) indicates that the use of cement or lime before the addition of the emulsion drive to a significant increase in the resistance of the mix. However the conserved strength after immersion is very low when lime is used. Consequently cement is preferred to lime. Addition of bitumen emulsion to the sample duplicates dry strength and increases significantly the strength after immersion comparing with those results in which only cement was used. This is an indication of longer durability of the bitumen emulsion pavement. The optimum cement content is 2% and optimum bitumen emulsion content is selected according minimum content required (3%).

Table 3. - Results of immersion-compression test with *Sample 2* (soils with petroleum spills) (NLT – 162 y 161).

Curing 24 h at room temperature and 4 days at 60ºC. Immersion procedure nº 1, 4 days at 49ºC						
Identification	10	11	12	13	14	15
PROPORTIONS						
Sample 2	100	100	100	100	100	100*
Emulsion	3	4	5	5		
Cement	2	2	2		2	2*
Water	3.0	2.6	2.2	2.2	4.0	4.0*
Dry strength, [kg/cm^2]	4.69	4.14	3.36	1.35	7.59	9.22
After immersion strength, [kg/cm^2]	2.96	2.70	3.07	0.46	5.87	
Conserved strength, [%]	63	65	91	34	77	
Relative Density [s.s.s.]	2.025	2.009	2.015	2.014	2.086	2.071

* These specimens were cured in wet chamber at 25ºC, 95% relative humidity for 7 days.

After the results obtained for *sample 1*, it was decided to use only cement to do the studies of *sample 2*. As can be seen in table 3 the strength obtained is lower than those obtained with *sample 1*. This is due to the presence of a higher quantity of hydrocarbon in the soil. In addition this hydrocarbon is lighter than those obtained from *sample 1*, because it has lower density. Hydrocarbons soft bitumen from the emulsion and it drive to a lower strength of the asphalt mix. However, with the addition of 2% of cement the minimum strength required was reached. In this case the optimum to manufacture the cold mixture was also 2% of cement and 3% of emulsion.

Table 4. - Results of immersion-compression test with Sample 2 (soils with petroleum spills) with 10/ 20 bitumen (NLT – 162 y 161).

Curing 24 h at room temperature and 4 days at 60ºC. Immersion procedure nº 1, 4 days at 49ºC			
ii. Ide	16	17	18
PROPORTIONS			
iii. S	100	100	100
Emulsion	3	4	5
Cement	2	2	2
Water	3.0	2.6	2.2
Dry strength, [kg/cm]^2	8.93	7.89	6.54
After immersion strength, [kg/cm^2]	5.80	5.60	6.15
Conserved strength, [%]	65	71	94
Relative Density [s.s.s].	2.025	2.009	2.015

If because of any reason were necessary to obtain higher strength one simple solution, as can be seen later, is to manufacture the emulsion with a harder bitumen, i.e. a 10/20 bitumen. In table 4 results when used the same formulae of emulsion, except that the bitumen used is a 10/20 grade instead the 80/100, are presented. As can be seen there is a significant increase in the strength. To manufacture this kind of emulsion it is necessary a lighter complicated plant, because it is necessary the use of pressure. However the advantage with respect to the hot mix technology is maintained.

Leaching laboratory method to investigate contaminant capability of the pavement has been performed on the specimens prepared with bitumen emulsion and HCS of the *sample 1* only, because it presents better pavement properties if it is compared with the use of cement as binder. The leaching material was analyzed as indicated above and results are shown in table 5. Data indicate lixiviation of hydrocarbons in specimens prepared with only cement as binder but not with bitumen emulsion. Metals analysis indicates that bitumen emulsion encapsulate some metals from cement (Fe, Li, Mg or

Ni) or from salts content in petroleum. Lixiviation of V, Ba or Mo from bitumen emulsion is produced and detected in analysis. These results indicate that bitumen from the emulsion encapsulates very effectively the contaminated soil and it is a technical and economic solution to pollution of soils by hydrocarbon.

Tabla 5.. - Leaching material analysis (Sample 1) with cement and bitumen emulsion and only with cement as binder.

Mixes	A	B	White
PROPORTIONS			
Sample 1	100	100	
Cement	2	2	
Emulsion	3		
ORGANIC COMPOUNDS			
Total Leachable organic compounds	4 ppm	6 ppm	-
Leachable petroleum hydrocarbons	<1ppm	4 ppm	-
METALS ANALYZED Li, Be, B, C, Na, Mg, K, Ca, Rb, Sr, Cs, Ba, Sc, Y, La Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Re, Fe,Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, Tl, In,Ga, Al, Si, P, S, Cl, Br, Te, Se, As, Sb, Ge, Sn, Pb y Bi. Next metals were detected: [mg/L]			
B	0.47	1.39	<0.09
Ba	0.44	0.12	<0.03
Ca	597	790	4.70
Fe	<0.02	0.17	<0.02
K	20	16	0.16
Li	<0.07	0.17	<0.07
Mg	1.10	34	1.18
Mo	0.13	<0.09	<0.09
Na	466	497	2.2
Ni	0.10	0.22	<0.08
Sr	2.45	4.06	<0.004
V	0.34	<0.08	<0.08

CONCLUSIONS

From the present work, the following conclusions can be drawn. Stabilized PCS with cement as binder presents poor strength and contaminant capability by leaching of hydrocarbons and metals from cement and petroleum oil. It is possible increase significantly the conserved strength after immersion and reduces the contaminant capability of soil with proposed solution (*utilization of cold asphalt technology)*. Data obtained indicates that cement is necessary to obtain minimum required strength. The optimum cement content is 2% and optimum bitumen emulsion content is selected according minimum content required (3%) but this conclusion depends on grain size distribution of HCS and the contaminant source.

Main conclusion is that using of cold technology is a cost and technical effective recycling technology but successful use of HCS as aggregate in light traffic pavements required a detailed study for each particular HCS.

REFERENCES

[1] Farhads Nadim, George E. Hoag, Shili Liu, Robert J. Carley and Peter Zack. Detection and remediation of soil and aquifer systems contaminated with petroleum products: an overview. Journal of Petroleum Science and Engineering 26, Issues 1-4 (2000) 169-178.

[2] Czarneki RC. Making use of contaminated soil. Civil Engineering 1988;58(12) 72-4

[3] Meegoda JN, Muller RT. Petroleum contaminated soils in highway construction. In: Symposium proceedings: recovery and effective reuse of discarded materials and by-products for construction of highway facilities, Denver, CO, 1993, p. 4-83–4-95.

[4] C.S. Poon, A critical review of evaluating procedures for stabilization/solidification process. In: P.L. Cote and T.M. Gilliam, Editors, Environmental aspects of stabilization/solidification of hazardous and radioactive wastes. STP 1033, ASTM (1989), pp. 114–124.

[5] Hijazi H, Pamukcu S. Possible re-use of petroleum-contaminated soils as construction material. Proceeding of the 22nd mid-atlantic industrial waste conference, Philadelphia, PA, p. 155–170.

[6] Meegoda JN, Ezeldin AS, Vaccari DA, Muller RT. Petroleum contaminated soils in highway construction. In: Proceedings of the 3rd materials engineering conference, infrastructure: new materials and methods of repair, San Diego, CA, 1994, p. 904–911.

[7] Hossam F. Hassam and col.. Potential uses of petroleum contaminated soil in highway construction. Construction and Building Materials 19, Issue 8, (2005) 646-652

[8] Taha, R and col.. An overview of waste materials recycling in the Sultanate of Oman. Resources, Conservation and Recycling 41 (2004) 293-306.

[9] NLT. I. Test Methods- Ensayos de carreteras.- Centro de Estudios y Experimentación de Obras Públicas (CEDEX). MOPT (Spain). Ed. Jun 1999

[10]ASTM Standads. Information on http://www.astm.org/Standard/index.shtml